California Environmental Protection Agency

Air Resources Board

Special Analysis Section
Northern Laboratory Branch
Monitoring and Laboratory Division

MLD SOP SAS 01

STANDARD OPERATING PROCEDURE FOR THE TOTAL VOLATILE MEASUREMENT OF CONSUMER PRODUCTS

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DISCLAIMER: Mention of any trade name or commercial product in Method 310 and associated Standard Operating Procedures does not constitute endorsement or recommendation of this product by the Air Resources Board. Specific brand names and instrument descriptions listed in the Standard Operating Procedures are equipment used by the ARB laboratory. Any functionally equivalent instrumentation can be used.

1 INTRODUCTION

This document describes a procedure for the measurement of the total weight percent of volatile organic compounds (VOCs) in the non-propellant portion of a consumer product as determined by U.S. EPA Method 24/24A and ASTM D2369-97. The mention of trade names or commercial products in this Standard Operating Procedure does not constitute endorsement or recommendation by the Air Resources Board (ARB) and are included as examples only.

2 SUMMARY OF METHOD

The gravimetric analysis is for the determination of total volatile material in a sample. An aliquot of product is weighed into an aluminum foil dish and heated in a forced-air oven at 110 ^{o}C for 60 minutes. The total volatile material is the difference in weight of the sample before and after heating. The total VOC is subsequently corrected for non-VOC, low vapor pressure and exempt compounds in the final weight percent calculation.

3 INTERFERENCE/LIMITATION

3.1 Certain consumer products may react with the aluminum weighing dishes. In these cases, substitute with Teflon petri dishes.

3.2 Products containing polymeric materials may exhibit weight loss not considered "volatile".

3.3 Substances considered "low vapor pressure" as defined in the consumer products regulation may volatilize under the conditions of this analysis. The total weight percent volatile content must be adjusted for this loss.

4 APPARATUS

4.1 Oven, forced draft, able to maintain a temperature of 110 $\pm$ 5 ^{o}C (ASTM Type II A or Type II B recommended).

4.2 Laboratory vented enclosure.

4.3 Analytical Balance, capacity of 100 g $\pm$ 0.0001 g.

4.4 Weighing Dishes

4.4.1 Aluminum Weighing Dishes, 58 mm x 18 mm w/ a smooth (planar) bottom surface (per ASTM 2369)

4.4.2 Teflon PFA Petri Dishes, 50 mm x 15 mm w/ a smooth (planar) bottom surface (per ASTM 2369)

4.5 Disposable Syringe, 3 - 5 ml, w/ caps

4.6 Desiccator

4.7 Wrist Action Shaker

4.8 Gloves, sharps resistant

4.9 Forceps

5 REAGENTS

5.1 Water, distilled, ASTM Type I

5.2 Acetone, reagent grade

5.3 Methanol, reagent grade

5.4 Trip Sample – 90% VOC

6 PROCEDURE

6.1 Label aluminum weighing dishes with identification numbers - two dishes are required per sample. Place aluminum dishes in a 110 ^{o}C oven for 60 minutes. Cool to ambient temperature in desiccator. Gloves shall be worn during all steps of this procedure to prevent weighing errors due to handling.

6.2 Remove the aluminum weighing dishes from desiccator with forceps. Weigh and record the empty aluminum dish weight, to the nearest 0.1 mg.

6.3 Mix the sample to ensure homogeneity. Using a syringe, withdraw approximately 3 ml of product. Wipe the sides of the syringe to remove any residual product. Cap and weigh the syringe with liquid sample. Dispense approximately 1 g of liquid sample into the aluminum dish. Cap and reweigh the syringe after sampling. Prepare replicate. If the sample in the dish does not form a thin film, add a small amount of acetone or methanol, and evenly disperse.

6.4 Put the dish with sample in the oven at 110 ^{o}C for one hour. Cool in desiccator to room temperature. Record the weight of the aluminum dish with residue. If the sample appears to be reacting with the aluminum dish, a Teflon dish should be substituted.

6.5 Calculate the total weight percent of volatile material in the sample in accordance with Section 8. If results of the replicate weight percent differ by more than one percent volatile material, repeat Section 6.

7 QUALITY CONTROL

7.1 The balance is calibrated daily, using the internal calibration program on the balance.

7.2 After the balance is calibrated it is checked using a 1.0 g ASTM Class 1 mass. The value is recorded on the gravimetric balance check chart. The 1.0 g weight should be within ±2sd of the expected value.

7.3 ASTM Type 1 water is used as a gravimetric oven check. The water is treated as a sample and carried through the procedure. If the oven is operating properly, the water sample will be calculated as 100 percent VOC. Record the value on the gravimetric oven check chart. The value should be ± 3 % of the calculated value.

7.4 In addition, a sample of known concentration designated as the Trip sample (90 % VOC ±3%) is carried through the analysis.

7.5 If results of the replicate weight percents differ by more than one percent volatile material, repeat Section 6

7.6 If the gravimetric oven check and/or the replicate gravimetric results are not within acceptable values, check the oven conditions and reanalyze the sample set.

7.7 The balance is calibrated semi-annually by a certified technician.

8 CALCULATIONS

8.1 Data Summary

8.1.1 A = Weight of empty aluminum dish to the nearest 0.1 mg, as determined by Section 6.2.

8.1.2 B = Weight of syringe w/ liquid sample to the nearest 0.1 mg, as determined by Section 6.3.

8.1.3 C = Weight of syringe after dispensing sample to the nearest 0.1 mg, as determined by Section 6.3.

8.1.4 D = Weight of cooled aluminum dish with sample residue to the nearest 0.1 mg, as determined by Section 6.4.

8.2 Equations

8.2.1 Weight (g) of Liquid Sample = [B] - [C]

8.2.2 Weight (g) of Residue = [D] - [A]

8.2.3 Total Volatile Sample, weight fraction = $\frac{([B] - [C]) - ([D] - [A])}{([B] - [C])}$

8.2.4 Relative Percent Difference = $\frac{(Dup\ 1) - (Dup\ 2)}{[(Dup\ 1) + (Dup\ 2)]/2} \times 100 percent$

APPENDIX A

Gravimetric Determination of Consumer Product Samples

1. The Sartorius MC1 analytical balance is used for the gravimetric analysis. The instrument is to be calibrated on a daily basis. Press F1 on the balance and the instrument will do an internal calibration.

2. A check of the accuracy of the balance is made using an ASTM Class 1 mass. Zero the balance. Using the forceps, remove the 1.0g ASTM Class 1 Calibration Mass and place it on the balance. When the reading becomes stable for 15 seconds, record the weight on the appropriate control charts to 5 places. If the weight is not within the control limits, then the balance should be re-calibrated as described in #1 above. After the calibration, re-weigh the ASTM mass.

3. Label the aluminum weighing dishes with identification numbers/marks. Two dishes are required per sample. Also include dishes for the gravimetric oven check and trip samples. The dishes are either aluminum foil (57 mm diameter x 10 mm high) with a flat bottom or teflon PFA petri dishes (58 mm diameter x 15 mm high) with a flat bottom. The teflon will be used in cases where the product may react with the aluminum dish.

4. Place the labeled aluminum weighing dishes in a 110 ^{o}C oven. After 60 minutes, remove the dishes from the oven and allow them to cool to ambient temperature in a desicator.

5. Each balance is connected to a PC to allow for automatic weight transfer. On the PC open the Network LimsLink V2.1. Once the software has finished opening, click on the “running man” icon. This allows you to run a method worksheet.

6. Select the worksheet SOP 300 Balance to run. This should be the default selection. Click on “new”.

7. Under “description”, enter the lab ID numbers for your sample set and under “operator name” enter in the first initial of your first name followed by your last name. Then click on “OK”.

8. Enter the following information into the worksheet :

   Under Sample Number
   Record your lab sample ID

   Under QC Type –

Enter “duplicate” for your duplicate sample.
Also enter your trip sample and gravimetric oven check sample in this column.

9. After all of your samples have been entered into the worksheet, select the options heading of the worksheet and click on expansion 2. The expansion 2 option adds the replicate sample to the worksheet. Under the worksheet heading Run # enter “1” or “2” to indicate the first and second replicates

10. With forceps, remove the weighing dishes from the desiccator and place them on a clean cookie sheet. On the PC, under the options heading select “collect 2, open”. This option will allow the weight reading from the balance to be transferred into the worksheet.

11. On the PC, place the cursor in the Pan Weight column for the first sample. Weigh the corresponding empty aluminum weighing dish to 0.1 mg and transfer the weight value to the worksheet by pushing the “print” button on the balance. Use the arrow keys to move to the next sample and repeat for all remaining samples.

12. Tare a clean 50 mL beaker. Mix the sample aliquot thoroughly either by shaking or vortexing.

13. Using a 3 ml disposable syringe, withdraw approximately 3 ml of the product, wipe the outer surface of the syringe with a Kimwipe to remove excess product. Cap and weigh the syringe by placing the syringe in the tared 50 ml beaker. Record the weight in the column marked syringe initial weight. Dispense approximately 1.0 ml of the sample into the labeled weighing dish. Cap and reweigh the syringe. Record the weight in the column syringe final weight. The difference is the actual amount of the product placed in the weigh dish.

14. The syringe final weight is also the syringe initial weight for the replicate sample.

15. Dispense approximately 1.0 ml of the sample into the weigh dish for the replicate as described in #13 above. Cap and reweigh the syringe. Record the weight as the syringe final weight. The difference is the actual amount of the product in the dish. Discard the syringe.

16. If the sample is too viscous (ex. solid or gel) use a transfer tube to dispense the sample. Draw up about 1.0 g of product, wipe the outside of transfer tube with a Kimwipe, and dispense the product directly into a tared weighing dish. For the syringe initial weight manually enter the value “2 x the sample weight” into the worksheet. For the syringe final weight manually enter the sample weight into the worksheet. These values need to be inputted into the worksheet in order for the program to calculate the sample weight correctly.

17. The weighing dishes with the sample in them are placed in the oven at 110 ^{o}C for 60 minutes. It is important that this time does not exceed $\pm$ 5 minutes. After 60 minutes, the weighing dishes with sample residue are removed from the oven and placed in a desiccator to cool to room temperature.

18. Weigh the aluminum weighing dishes with sample residue and record the weight in the worksheet under the column heading “weight pan + residue”.

19. Any observations regarding the sample residue should be noted in the analyst's notebook.

20. Calculations:

    a. Weight of sample = (syringe initial weight) - (syringe final weight)

    b. Weight of residue = (weight of dish w/ sample residue) - (weight of empty dish)

    c. Percent volatile (w/w) = $100 \times \frac{[(\text{weight sample}) - (\text{weight residue})]}{\text{weight sample}}$

21. If the results between the two replicate analyses differ by more than one percent VOC, repeat the analyses.

22. Verify that the gravimetric oven check value is 100% VOC $\pm$3 %.

23. Verify that the trip sample value is correct (90 % VOC $\pm$ 3 %).

24. The gravimetric results are reported as the average of the two replicates.

******NOTES******

1. Gloves must be worn during all steps of this procedure where weights or weighed objects are dealt with.

2. If the sample in the dish does not form a thin film, add 2 ml of acetone or methanol and evenly disperse.

3. Aluminum dishes can be used for most products. However where there may be a reaction with the aluminum, teflon dishes can be substituted.

**DO NOT EXCEED THE TIME FOR THE SAMPLES TO STAY IN THE OVEN!!

SOP REVISION HISTORY

Date	Version	Notes
October 10, 1996	1.0	Additions to the QC section the addition of the trip sample and clarify the calibration of the balance.
March 10, 1998	2.0	Adjusted document font to Times New Roman 12. Inserted appendix A formerly a stand-alone document.
October 26, 2000	3.0	Renumbered to new Section Number, Change Font to Arial 12.
June 27, 2003	1.4	Added procedure for use of Network LimsLink V2.1 software into Appendix A. Corrected version enumeration.